

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁴ : A61K 7/075	A1	(11) International Publication Number: WO 89/ 04163 (43) International Publication Date: 18 May 1989 (18.05.89)
(21) International Application Number: PCT/GB88/00962 (22) International Filing Date: 7 November 1988 (07.11.88) (31) Priority Application Number: 8726439 (32) Priority Date: 11 November 1987 (11.11.87) (33) Priority Country: GB (71) Applicant (for all designated States except US): DOW CORNING LIMITED [GB/GB]; Inveresk House, 1 Aldwych, London WC2R 0HF (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : DONKERS, Anne-mieke, Constantia, Maria [BE/BE]; Koetsweg 43, B-1200 Kessel-Lo (BE). WRIGHT, Shirley, Elizabeth [GB/GB]; 10 Goodwick Close, Barry, South Glamorgan (GB).	(74) Agent: BULLOWS, Michael; Dow Corning Limited, Cardiff Road, Barry, South Glamorgan CF6 7YL (GB). (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US. Published With international search report.	

(54) Title: CONDITIONING COMPOSITIONS

(57) Abstract

An improved conditioning composition for e.g. human hair is formed by admixture of an aqueous emulsion of a polydiorganosiloxane which is preferably a linear polydimethylsiloxane or polymethylphenylsiloxane, and a quaternary ammonium silane of the general formula (ii) $R^3_3SiR^4N^+(R^5)_3X^-$ having preferably one aliphatic C_{8-18} group and 2 aliphatic C_{1-5} groups linked to the N atom. The composition can be used as a rinse conditioner or may be incorporated in a shampoo composition.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland				

- 1 -

CONDITIONING COMPOSITIONS

This invention is concerned with conditioning compositions and is particularly concerned with conditioning compositions for human hair.

5 It has become a common practice to wash human hair frequently in order to clean it, and it is normal to use for this purpose a shampoo containing a synthetic detergent. There are many shampoo formulations available which are effective to clean the hair, but generally the detergents employed have a tendency to leave the hair in a
10 condition such that it is difficult to comb when wet and somewhat unmanageable when dried. It has therefore also become a practice to apply conditioner materials to the hair which are intended to improve the properties of the shampooed hair. These materials may be applied to the hair
15 in admixture with the shampoo or applied to the wet shampooed hair as a separate conditioner, for example as a rinse.

Various proposals have been made concerning the formulation of compositions intended for use, for example,
20 on human hair with a view to conditioning the hair, i.e. imparting to the hair one or more desirable properties, for example, ease of combing or detangling of wet hair, or ease of combing, lustre, a fullness or body accompanied by a certain liveliness, manageability and avoidance of static
25 in the dried hair. Such compositions may take the form, for example, of shampoos, conditioners or rinses, and all such compositions are referred to herein as conditioning compositions. It is a common practice to employ surfactants such as stearyl dimethylbenzylammonium chloride,
30 cetyltrimethylammonium bromide and dimethylbis(hydrogenated tallow)ammonium chloride, for their hair conditioning

- 2 -

properties. These materials are effective in many respects but in order to provide some of the desired properties, it is necessary to employ significant amounts of the surfactant and as a consequence other properties are impaired.

5 This in turn has led to proposals to include significant proportions of other selected ingredients in conditioning compositions to impart softness and other properties to the hair. It has been proposed, for example, to employ certain polydiorganosiloxanes to impart increased softness to the
10 hair. Other proposals have been made to employ in hair treating compositions certain organosilicon compounds having quaternary ammonium salt groups. For example, hair treating compositions comprising certain silanes or polysiloxanes having quaternary ammonium groups in combination
15 with polysiloxanes having certain amino groups are described and claimed in G.B. patent specification 2 144 329. These compositions are effective to provide a variety of desirable properties to shampooed hair but it is recommended that they are not used frequently on the hair due to a tendency of the polysiloxanes having amino groups to adhere strongly to the hair for a considerable time and to resist removal during normal shampooing. Also, the polysiloxanes having siloxane units including quaternary ammonium salt groups generally require a series of preparation steps
25 and their manufacture can be costly.

It is one of the objects of the present invention to provide an improved conditioning composition. It is another of the objects of the invention to provide an improved method of treating hair.

30 We have now found that a conditioning composition capable of imparting a range of beneficial properties to human hair may be provided by an aqueous composition based on certain selected polydiorganosiloxanes and selected silanes having quaternary ammonium salt groups.

- 3 -

The present invention provides in one of its aspects a conditioning composition formed by admixture of components comprising (a) an aqueous emulsion of a polydiorganosiloxane having units of the general formula $R'R_2SiO_{\frac{1}{2}}$ and $R_aSiO_{\frac{4-a}{2}}$ in which R is selected from the group consisting

of alkyl and aryl groups having no more than 8 carbon atoms, R' is selected from R groups and hydroxyl and a is an integer with a value of from 0 to 2, with (b) a quaternary ammonium compound characterised in that the quaternary ammonium compound is a quaternary ammonium silane of the general (ii) $R^3_3SiR^4N^+(R^5)_3X^-$ in which each R^3 is selected from the group consisting of alkyl groups having up to 5 carbon atoms in their chain, a hydroxyl group, alkoxy groups, alkoxyalkoxy groups having less than 12 carbon atoms, and a trimethylsiloxy group, R^4 represents a divalent aliphatic hydrocarbon group having from 2 to 10 carbon atoms in its chain linking the silicon and nitrogen atoms and composed of carbon, hydrogen, optionally oxygen in the form of hydroxyl and optionally oxygen in the form of ether linkages, each R^5 represents a monovalent hydrocarbon group, from 1 to 2 groups R^5 having an aliphatic chain composed of on average from 8 to 18 carbon atoms and from 1 to 2 groups R^5 having an aliphatic chain composed of not more than 5 carbon atoms and X^- represents a monovalent anion.

Component (a) is an oil-in-water emulsion of a polydiorganosiloxane compound. Suitable polydiorganosiloxanes are those which can be provided in emulsions either by emulsion polymerisation or by mechanical emulsification. Preferred polydiorganosiloxanes are linear polymers wherein a has a value of 2 and which have the average general formula (i) $R'SiR_2[OSiR_2]_nOR_2SiR'$, wherein R and R' are as

- 4 -

defined above and n is an integer. The groups R are preferably at least predominantly methyl but may include phenyl or other aromatic groups as aforesaid. Polydiorganosiloxanes in which at least substantially all R

5 groups are methyl groups preferably have a viscosity of at least 1000 mm²/s at 25°C and preferably less than about 300,000 mm²/s; preferably they have a viscosity of from 10,000 to about 200,000 mm²/s at 25°C, most preferably from 12,500 to 100,000 mm²/s at 25°C. Polydiorganosiloxanes in

10 which more than about 10% of the R groups are phenyl and less than 90% are alkyl groups preferably have a viscosity in the range of about 10 to about 1000 mm²/s at 25°C. The emulsion, in which the polydiorganosiloxane is provided may be made by mechanically emulsifying a polydiorganosiloxane

15 of required viscosity according to methods which are well known in the art. Polydiorganosiloxanes which may be thus emulsified are well known, and many are commercially available. They may be prepared for example by the hydrolysis of halogenosilanes or by equilibration of cyclic diorgano-

20 siloxanes with monofunctional silanes. Alternatively the emulsion may be made by emulsion polymerisation, as is described for example in British Patent Specification 992 087. The latter method is particularly preferred for the higher viscosity polydiorganosiloxanes. Emulsions made

25 by the emulsion polymerisation technique are usually more stable and have a smaller particle size than the emulsions which are made by mechanical emulsification. Polydiorganosiloxanes made via the emulsion polymerisation technique usually have a structure in which each R' represents a

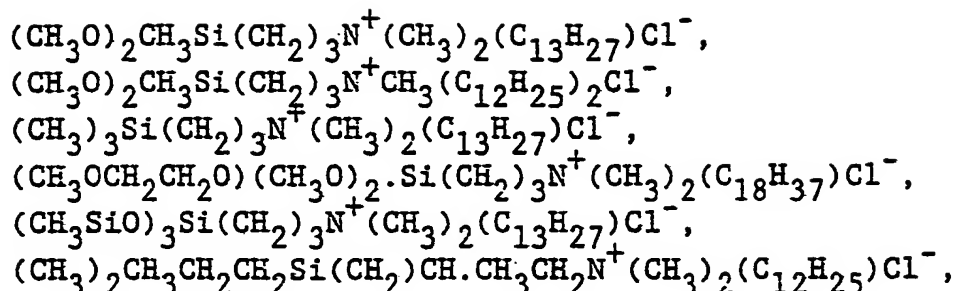
30 hydroxyl group. Emulsions which are useful in the present invention may have a solids content of up to about 75%, but preferably contain from about 10% to about 40% by weight polydiorganosiloxane. The amount of emulsion (a) in a

- 5 -

composition according to the invention is such that up to 2% by weight of the polydiorganosiloxane is utilised in the composition although it is preferred to use no more than 1% of the polydiorganosiloxane if its viscosity is in the more preferred ranges mentioned above.

In a composition according to the present invention the component (b) is a quaternary ammonium silane of the formula (ii). Preferably at least one of the groups R^3 is an alkyl group, preferably a methyl group and up to two of the groups R^3 are alkoxy groups, preferably methoxy groups. The quaternary ammonium silanes are known materials and may be prepared in various ways, for example as disclosed in G.B. patent specifications 1 117 592 and 2 107 715. We prefer to prepare them from the corresponding tertiary amine and chlorosilane, trialkyl chlorosilanes are preferred over those containing readily hydrolysable groups, for example alkoxy and alkoxyalkoxy groups, thus avoiding production of disiloxanes and trisiloxanes during conversion of the silane to the quaternary ammonium salts. The group R^4 may be for example $-(CH_2)_3-$, $-(CH_2)_4-$, $-CH_2CH_2CHCH_3CH_2-$ or $-(CH_2)_6-$ and the groups R^5 may be chosen for example from methyl, ethyl, propyl, decyl, dodecyl, tetradecyl and octadecyl. Preferably one only of the groups R^5 has a longer aliphatic chain. We prefer that two of the groups R^5 are methyl groups and one of them has an aliphatic chain having on average about 12 to 14 chain carbon atoms. The nature of the anion X^- influences the solubility of the silane; whilst many organic and inorganic anions may be employed depending on the surfactant used in the emulsion, for example acetate, bromide and iodide, we prefer to employ the chloride ion. Examples of suitable quaternary ammonium silanes include those of the formulae

- 6 -



Component (b) of a composition according to the invention is water soluble and may be readily incorporated with component (a) by a simple mixing procedure.

Components (a) and (b), when mixed in the required proportions provide an aqueous emulsion which may be readily supplied to the hair. The emulsion may be formulated into a form in which it is stable for a short period but unless appropriate surfactants and stabilizers are included in the formulation, the emulsion is likely to be unstable in storage and it is then preferable to store the components separately and to mix them in desired proportions shortly before use.

A composition according to the invention may, and preferably does, contain at least one surfactant which functions to stabilize the emulsion and maintain the polydiorganosiloxane in the dispersed state in the aqueous medium. The nature of the surfactant is not critical; preferably it is cationic or nonionic. Examples of surfactants are aliphatic fatty amines and their derivatives e.g. octadecylamine acetate and quaternary ammonium halides, sulphonic acids e.g. dodecyl benzene sulphonic acid, ethylene oxide adducts of octyl or nonyl phenols e.g. octylphenoxy polyethoxyethanol, condensation products of aliphatic alcohols and ethylene oxide, monoesters of alcohols and fatty acids e.g. sodium lauryl sulphate glyceryl stearate, sorbitan monolaurate and polyoxyethylenemonostearate, and polyvinyl alcohol. The

- 7 -

surfactant component is generally employed in amounts of about 0.01% to about 5% by weight of the composition.

5 In a composition according to the invention, the silane (b) is preferably present in excess of about 0.25% by weight of the composition in order to achieve the desired low level of static for the treated hair. Larger proportions may be used to give increased static control but it is generally not necessary to employ more than about 5% of the silane in the composition. The polydiorgano-
10 siloxane provided in component (a) is present principally to contribute softness and related properties. When using the lower molecular weight polydiorganosiloxanes, the amount employed is greater than when the higher molecular weight polydiorganosiloxanes are employed. In order to
15 secure the desired blend of properties we prefer to employ the materials of the general formulae (i) and (ii) in proportions such that the ratio by weight of polydiorgano-siloxane:silane is less than about 2.5:1, more preferably lies in the range 0.1:1 to 2:1. If the ratio lies outside
20 this range, the reduction in static and the combination of properties achieved is inferior.

It is not necessary to include any ingredients in a conditioner composition intended for use as a rinse for the hair in addition to components (a) and (b). However, if
25 desired, the composition may include other ingredients as stabilisers, for example non-ionic surfactants as afore-said, thickeners e.g. carboxymethyl cellulose, hydroxypropyl cellulose and guar gum, colorants, perfumes, bactericides, solvents, preservatives, and conventional hair
30 conditioning ingredients e.g. handle modifiers eg fatty acid salts esters and ethers and long chain alkyl alcohols, waxes, oils and organic quaternary compounds. In addition, the composition may be formulated as a shampoo by the

- 8 -

inclusion of suitable sequestering agents and detergents for the cleaning of hair, for example those based on fatty alcohols e.g. lauryl and myristyl alcohols, or fatty alcholethoxylates. Examples of such detergents are sodium
5 lauryl sulphate, sodium lauryl ether sulphate, ammonium lauryl sulphate and triethanolamine lauryl sulphate. The surfactant chosen for the emulsification of the polysiloxane may in some cases function also as the detergent component of the shampoo formulation. When so formulated,
10 the proportion of the surfactant used will normally be much larger than the amount used to provide the stability of the emulsion.

Also included within the scope of the invention is a process for the treatment of hair which comprises applying
15 thereto a composition according to the invention. The treatment is preferably done after the hair has been shampooed and the shampoo rinsed off, but it may be done simultaneously with the shampooing of the hair, the latter being more appropriate when a composition according to the
20 invention is formulated as a shampoo.

Compositions according to the present invention allow the formulation of hair conditioning compositions as a shampoo or as a rinse for treating shampooed hair, using a
25 minimal number of ingredients in comparatively small quantities, still providing a desirable conditioning effect on human hair and, in particular, ensuring a low level of static electricity in the treated hair. In addition, the composition may be easily washed from the treated hair in a
30 normal shampooing of the hair.

In order that the invention may become more clear, there now follows a description of example compositions selected to illustrate the invention. Unless otherwise specified, all parts mentioned are parts by weight.

- 9 -

A first aqueous emulsion was prepared by emulsion polymerisation of cyclic polydimethylsiloxanes in presence of an alkyl benzene sulphonic acid to provide an emulsion of 35 parts of a first polydiorganosiloxane namely a dimethylhydroxysiloxy end blocked polydimethylsiloxane having a viscosity at 25°C of 100,000 mm²/s, dispersed in water and neutralised with triethanolamine, together with minor amounts (i.e. less than 5% of the composition, and preferably less than 3% of the composition) of preservative and a non-ionic emulsifier as stabilizer and 53 parts water.

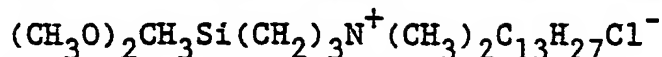
A second aqueous emulsion of 35 parts of a second polysiloxane namely trimethylsiloxy end blocked polydimethylsiloxane having a viscosity at 25°C of 12,500 mm²/s was prepared by emulsion polymerisation in presence of an alkyl benzene sulphonic acid in water and neutralised with triethanolamine, together with minor amounts of preservative and a non-ionic emulsifier as stabilizer and 53 parts water.

A third aqueous emulsion of 60 parts of a third polysiloxane namely a trimethylsilyl end blocked polydimethylsiloxane having a viscosity at 25°C of about 350 mm²/s, was formed by dispersing the polysiloxane in about 35 parts water in presence of minor amounts of a non-ionic surfactant, sodium lauryl sulphate and preservatives.

A fourth aqueous emulsion of 1 part of a fourth polysiloxane namely a trimethylsiloxy end blocked polysiloxane consisting of about five dimethyl siloxane units and about five phenylmethyl siloxane units and having a viscosity at 25°C of 100 mm²/s, was formed by dispersing the polysiloxane in water in presence of minor amounts of a thickener and cetyl alcohol.

- 10 -

These emulsions were mixed with the silane



and with a non-ionic self emulsifying wax in quantities as shown in Table 1. Various comparative compositions were also prepared using components as shown in Table 1. The resulting compositions were used to treat swatches of virgin European hair and their ability as conditioning compositions was assessed by reference to their ability to ease the combing of hair, both when wet after shampooing, and when dry, for their ability to reduce static, and for the handle (feel and body) they impart to the hair. The tests were carried out as follows. A hair swatch (virgin European brown hair) was wetted and washed twice using a shampoo, based on 20% sodium lauryl ether sulphate and 3.5% of linoleic diethanolamide. The hair swatch was rinsed well in running water. Then 5ml of the composition under examination per 7.8g of hair was applied to the swatch. After 1 minute, the hair was combed in order to obtain an equal spreading of the conditioner, and the hair swatch was rinsed for 15 seconds. When the excess of water had been removed, the hair swatch was tested for wet combability. This was done by passing a fine plastic comb through the hair and assessing the ease of combing on a scale of 0 to 10 with 0 being allocated to swatches combable only with difficulty or not at all and 10 being allocated to swatches showing excellent ease of combing. Results are shown in Table 2 in the column "Wet Comb I". After the hair had been detangled, the combability was again assessed in the same way according to the same scale. Results are shown in Table 2 in the column "Wet Comb F". The hair swatch was then dried in an air-circulating oven at 70°C for one hour. When the hair had cooled to room temperature dry combability was assessed in the same way as the wet combability,

- 12 -

TABLE 2

Composition		Wet Comb		Dry Comb		Body (%)	Static	Handle
		I	F	I	F			
Comparative								
5	1	2	4	4	4	100	5+	(a)
	2	3	7	3	6	75	0	(b)
	3	3	6	3	6	25	0	(c)
	4	3	7	4	6	20	5	(d)
	5	3	8	5	7	50	4	(e)
10 Illustrative								
	1	5	8	6	7	50	2	(f)
	2	3	7	6	8	50	2	(g)
	3	3	8	6	7	133	2	(h)
	4	4	9	6	7	50	1	(i)
15	5	4	9	6	8	50	5+	(j)
	6	5	9	6	7	60	2	(j)
	7	4	9	5	7	50	0	(j)
	8	3	7	6	8	50	0	(k)
	9	3	7	4	6	133	4	(l)
20	10	5	9	6	8	100	0	(m)
(a) average								
(b) bodied, slightly heavy but slick								
(c) bodied, slightly heavy								
(d) slick, bad static								
25	(e) silky soft, dry ends							
	(f) smooth, soft, silky							
	(g) good body, lively, nice							
	(h) silky, smooth bodied							
	(i) slick, bouncy							
30	(j) smooth, silky							
	(k) slightly heavy							
	(l) soft, slightly heavy							
	(m) very soft							

- 11 -

results of the initial combing and final combing being recorded in Table 2 in the columns "Dry Comb I" and "Dry Comb F" respectively. The percentage increase in bulk size was measured and recorded in Table 2 as "Body". The static of the hair was assessed by combing the dry hair five times downwards with a plastic comb, and comparing the angle at which the hair spreads out before and after the combing. Performance of the compositions in this test was ranked on a scale 0 to 5 with 0 recording total absence of static. The handle was assessed by feeling the hair and considering its softness, silkiness and body. This test was carried out by a panel of people and the average result is recorded in Table 2.

TABLE I

15	Composition	Component(a)				Component(b)		Ratio
		Aqueous Emulsion				Wax		
	Comparative	1	2	3	4			
	1	0	0	0	0	5	0	-
	2	0	0	0	0	5	0.5	-
20	3	0	0	0	0	5	1.0	-
	4	1	0	0	0	5	0	-
	5	0	2.5	0	0	5	0	-
	Illustrative							
	1	2.5	0	0	0	5	0.5	1.75 :1
25	2	1.0	0	0	0	5	0.25	1.40 :1
	3	1.0	0	0	0	5	1.0	0.35 :1
	4	0.5	0	0	0	5	1.0	0.175:1
	5	0	2.5	0	0	5	0.25	3.5 :1
	6	0	2.5	0	0	5	0.5	1.75 :1
30	7	0	2.5	0	0	5	1.0	0.875:1
	8	0	2.5	0	0	5	2.5	0.35 :1
	9	0	0	2.0	0	5	0.5	2.4 :1
	10	0	0	0	1.0	0	1.0	1.0 :1

- 13 -

The results show that good conditioning benefits can be achieved by use of emulsions containing a polydimethylsiloxane and a quaternary ammonium silane. The comparative compositions 4 and 5 (which contained the polysiloxane and no silane) demonstrated good wet and dry combing properties but poor static control. The comparative compositions 2 and 3 (which contained the silane but no polysiloxane) demonstrated static control but poor conditioning in other respects. The illustrative examples all demonstrated a good combination of these properties, the more preferred compositions demonstrating good combinations of properties, including a low level of static to a surprisingly high level, indicating synergy of the combined ingredients. The combination of beneficial properties obtained on treated hair is most marked when using illustrative compositions 1, 2, 3, 4, 6, 7 and 8, in which compositions the ratio of polydiorganosiloxane:silane lies in the range 0.1:1 to 2.0:1

- 14 -

CLAIMS

1. A conditioning composition formed by admixture of components comprising (a) an aqueous emulsion of a polydiorganosiloxane having units of the general formula $R'R_2SiO_{\frac{1}{2}}$ and $R_aSiO_{\frac{4-a}{2}}$ in which R is selected from the group consisting of

alkyl and aryl groups having no more than 8 carbon atoms, R' is selected from R groups and hydroxyl and a is an integer with a value of from 0 to 2, with (b) a quaternary ammonium compound characterised in that the quaternary ammonium compound is a quaternary ammonium silane of the general (ii) $R^3_3SiR^4N^+(R^5)_3X^-$ in which each R^3 is selected from the group consisting of alkyl groups having up to 5 carbon atoms in their chain, a hydroxyl group, alkoxy groups, alkoxyalkoxy groups having less than 12 carbon atoms, and a trimethylsiloxy group, R^4 represents a divalent aliphatic hydrocarbon group having from 2 to 10 carbon atoms in its chain linking the silicon and nitrogen atoms and composed of carbon, hydrogen, optionally oxygen in the form of hydroxyl and optionally oxygen in the form of ether linkages, each R^5 represents a monovalent hydrocarbon group, from 1 to 2 groups R^5 having an aliphatic chain composed of on average from 8 to 18 carbon atoms and from 1 to 2 groups R^5 having an aliphatic chain composed of not more than 5 carbon atoms and X^- represents a monovalent anion.

2. A composition according to claim 1 characterised in that the polydiorganosiloxane has the average general formula (i) $R'SiR_2[OSiR_2]_nOR_2SiR'$ wherein n has a value such that the polydiorganosiloxane has a viscosity of less than 300,000 mm²/s.

3. A composition according to Claim 2 characterised in that the R groups are methyl groups and n has a value such that the polydiorganosiloxane has a viscosity of at least 1000 mm²/s.

- 15 -

4. A composition according to Claim 3 characterised in that when each R' represents a hydroxyl group \underline{n} has a value such that the polydiorganosiloxane has a viscosity of about 100,000 mm²/s and when each R' represents a methyl group \underline{n} has a value such that the polydiorganosiloxane has a viscosity of about 12,500 mm²/s.

5. A composition according to Claim 2 characterised in that more than 10% of groups R are phenyl groups and in that \underline{n} has a value such that the polydiorganosiloxane has a viscosity in the range 10 to 1000 mm²/s

6. A composition according to Claim 1 characterised in that the polydiorganosiloxane provides up to 2% by weight of the composition.

7. A composition according to Claim 1 characterised in that the silane has the formula
 $(\text{CH}_3)(\text{CH}_3\text{O})_2\text{Si}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{C}_{13}\text{H}_{27}\text{Cl}^-$.

8. A composition according to Claim 1 characterised in that the silane (b) provides up to 5% by weight of the composition.

9. A composition according to Claim 1 characterised in that the ratio by weight of polydiorganosiloxane:silane is less than 2.5:1.

10. A composition according to Claim 9 characterised in that the ratio by weight of polydiorganosiloxane:silane lies in the range 0.1:1 to 2.0:1.

- 16 -

11. A method of treating human hair comprising the step of applying to the hair a composition according to Claim 1 simultaneously with, or subsequent to, the steps of shampooing, and/or rinsing the hair.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 88/00962

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁴ : A 61 K 7/075																	
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 20%; border-bottom: 1px solid black;">Classification System</td> <td style="border-bottom: 1px solid black;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">IPC⁴</td> <td style="padding: 5px;">A 61 K</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC ⁴	A 61 K											
Classification System	Classification Symbols																
IPC ⁴	A 61 K																
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category *</th> <th style="width: 60%; border-bottom: 1px solid black;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 30%; border-bottom: 1px solid black;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;">GB, A, 2173515 (BEECHAM) 15 October 1986 see claims</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-11</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;">EP, A, 0179347 (REVLON) 30 April 1986 see claims</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1,6,7</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;">GB, A, 2144329 (DOW) 6 March 1985 see claims; examples 1-3 cited in the application</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-11</td> </tr> <tr> <td colspan="3" style="text-align: center; padding: 10px;">-----</td> </tr> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	Y	GB, A, 2173515 (BEECHAM) 15 October 1986 see claims	1-11	Y	EP, A, 0179347 (REVLON) 30 April 1986 see claims	1,6,7	Y	GB, A, 2144329 (DOW) 6 March 1985 see claims; examples 1-3 cited in the application	1-11	-----		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³															
Y	GB, A, 2173515 (BEECHAM) 15 October 1986 see claims	1-11															
Y	EP, A, 0179347 (REVLON) 30 April 1986 see claims	1,6,7															
Y	GB, A, 2144329 (DOW) 6 March 1985 see claims; examples 1-3 cited in the application	1-11															

<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 50%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search 3rd February 1988 </td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;"> Date of Mailing of this International Search Report 22.02.89 </td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;"> International Searching Authority EUROPEAN PATENT OFFICE </td> <td style="border-bottom: 1px solid black; padding: 5px;"> Signature of Authorized Officer P.C.G. VAN DER PUTTEN </td> </tr> </table>			Date of the Actual Completion of the International Search 3rd February 1988	Date of Mailing of this International Search Report 22.02.89	International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer P.C.G. VAN DER PUTTEN											
Date of the Actual Completion of the International Search 3rd February 1988	Date of Mailing of this International Search Report 22.02.89																
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer P.C.G. VAN DER PUTTEN																

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 8800962
SA 25157

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 15/02/89. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2173515	15-10-86	None	
EP-A- 0179347	30-04-86	US-A- 4567039	28-01-86
		JP-A- 61097209	15-05-86
		AU-A- 4839585	17-04-86
GB-A- 2144329	06-03-85	FR-A, B 2549720	01-02-85
		DE-A- 3427674	07-02-85
		JP-A- 60056916	02-04-85
		US-A- 4601902	22-07-86
		CA-A- 1245560	29-11-88